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Towards Applications of Quantum Dots: Surface Modification and Novels Electronic Properties

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Introduction

The possibility of quantum confinement causing the intense visible luminescence seen in porous Si, first mentioned by Canham in 1991,[1] led to enormous interest in that material. The large blue-shift in the band gap and increase in luminescent efficiency attributed to quantum confinement in porous Si, while still controversial, continues to fuel research on colloidal Si nanoparticles prepared by sonicating porous Si,[2-4] and by solution chemistry.[5-11] This interest continues, and has led naturally to an interest in colloidal Ge nanoparticles, since the elements are both indirect gap semiconductors, and the exciton of Ge has a larger Bohr radius.[12] The earliest preparation of Ge nanoparticles by a colloidal chemistry method started as a continuation of the previous work on Si, but required either high temperatures and pressures,[10] or laser annealing[13] to produce crystalline nanoparticles. There has been only limited work on colloidal Ge nanoparticles prepared by sonicating porous Ge,[14] with interest instead focused primarily on solution preparation of colloidal Ge nanoparticles.

The metathesis of the Zintl salts NaT, KT, and Mg_2T with TCl_4 (where T =Si or Ge) in boiling glymes has been used to prepare nanoparticles.[9,15,16] A key feature of this technique is the ability to control the surface termination of the nanoparticles prepared; since a large excess of the TCl_4 is used in the reaction, chloride anions remain on the surface of the nanoparticles. Since they react with chloride anions, RMgX (X= Cl or Br) or LiR reagents may be used to prepare nanoparticles with a desired surface termination. Continuing research has demonstrated the utility of this method in preparing crystalline

Ge nanoparticles in reasonable quantities with excellent stability and some provision for size control.

In the inverse micelle preparation of Si or Ge nanoparticles, both size control and size separation are incorporated into the preparative method. The partial separation of the halide salt and reductant into hydrophilic and hydrophobic regions of the inverse micelles permits some control over size distribution, which is greatly enhanced by the use of HPLC to size-separate the nanoparticles. In essence, TX_4 (X = Cl, Br, or I) was more soluble in the tetrahydrofuran (THF) portion of inverse micelles formed in THF/octane or THF/decane mixtures than in the hydrocarbon portion of the reaction mixture. The micelles form at the interface of the THF and alkane phases, with aliphatic polyethers or quaternary ammonium salts acting as phase transfer catalysts and stabilizing the micellar phase. Small regions of THF/TX_4 are formed with octane or decane separating them. This was followed by the introduction of the reductant, typically 1 M $LiAlH_4$ in THF. The micelles determine the size of nanoparticles produced, though thinking of micelles as pores or cavities is an oversimplification. Rather than act as cavities, which directly limit the size of the nanoparticles, the micelles slow the rate of reaction, separating crystallite nucleation from growth.

Synthesis

$$GeCl_4 + Mg_2Ge \rightarrow Ge_{diam} + MgCl \qquad (1)$$

$$SiCl_4 + Mg_2Si \rightarrow Si_{diam} + MgCl \qquad (2)$$
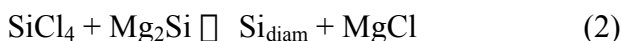
Due to the sensitivity of these reactions to air and water all manipulations were carried out under dry Ar gas, using standard Schlenk line techniques,[17] or in a glovebox filled with dry N_2. The reaction mixture (TMg_2, where T=Si or Ge) in aliphatic polyether solvents was heated to reflux, and formed a blue-gray opaque suspension. As the reaction began to reflux, TCl_4 was added dropwise during which time the reaction mixture became a clear to light-yellow suspension with a white precipitate, presumably $MgCl_2$. The reaction mixture was allowed to cool to room temperature, and excess TCl_4 was removed by evacuation through a trap cooled with liquid nitrogen. After removing any excess TCl_4, a RMgBr (where R = aliphatic, aromatic groups) was added by anaerobic syringe. The reaction mixture warmed slightly and more white precipitate formed immediately, indicating a reaction between the Grignard reagent and the nanoparticle surface. The reaction mixture was filtered to remove the precipitate, and extracted. The extracts were combined and concentrated using a rotary evaporator. The dried nanoparticles were characterized by FTIR, HRTEM and solid-state NMR spectroscopy. Suspensions of nanoparticles were characterized by photoluminescence spectroscopy. Yields of germanium and silicon nanocrystals were improved to exceed those currently published in the literatre.[13,18,19]

The inverse micelle preparation of nanoparticles has been investigated and it has been established that the micelle is not vital to the reaction. Silicon nanocrystals can be prepared by reducing the rate of reaction.

$$SiCl_4 + LiAlH_4 \rightarrow Si_{diam} + LiCl + AlCl_3 \qquad (3)$$

Surface Enhancement

For the chloride terminated species: We have shown that the chloride can be readily reacted to give organic species on the surface. Further manipulation of the surface organic group can be achieved by standard organic reactions. For example, reaction between p-chlorophenyl terminated nanocrystals with RLi or RMgBr has been demonstrated, as shown in equation 4. In which the surface is modified by replacement of the Cl with an organic group attached to the aromatic ring.

$$Ge_{diam}(C_6H_4)Cl + RMgBr \rightarrow Ge_{diam}(C_6H_4)R \qquad (4)$$

$$Ge_{diam}(CH_2COO^tBu) + H^+ \rightarrow Ge_{diam}(CH_2COOH) \qquad (5)$$

Surface modification have also been achieved through the use of protecting groups such as the t-butyl group for the carboxylic acid shown in Equation 5.

For the hydride terminated species: The reduction of silicon tetrachloride with $LiAlH_4$ results in a hydride-covered surface, which is highly reactive and susceptible to

oxidation. To stabilize the surface we have investigated the use of standard

hydrosilylation chemistry used on porous silicon to covalently attach organic groups.

Surface modification of Si nanocrystals is achieved by Lewis acid catalyzed

hydrosilylation with alkynes, as seen in equation 6.

$$Si_{diam} + EtAlCl_2 + HC \equiv CR \rightarrow Si_{diam}(C=CR) \qquad (6)$$

This reaction is only partially successful in protecting the nanocrystals from oxidation as

they do oxidize over a period day when exposed to the atmosphere.

Characterization and Discussion

A range of characterization tools has been employed to fully characterize the silicon and

germanium quantum dots produced and a summary of the data is given. The infrared

spectra in Figure 1 demonstrate that the surface termination protects the nanoparticle

from oxidation which is supported by the lack of Ge-O or Si-O stretch at 870-910 cm^{-1}

appearing in either spectrum shown. Additionally, the spectra of both samples fit well

with spectra expected for the organosilanes and organogermanes.

For most samples, solution state NMR has been obtained to verify the presence of the

organic groups on the surface of the nanocrystals. However in some cases solid state ^{13}C

cross polarization/magic angle spinning (CP/MAS) NMR spectra have been obtained as

shown in Figure 2. Only carbon atoms with protons directly attached give a signal in the

CP/MAS experiment, so these ^{13}C resonances are not seen in Figure 2. Since the mirror

plane from the Ge-C bond through the C-Cl bond splits the ring into 2 sets of equivalent C atoms, only 2 resonances are seen. The broad center peaks near 130 and 133 ppm and spinning sidebands demonstrate the hindered rotation of the chlorophenyl groups attached to the nanoparticle surface. This hindered rotation again shows that the organic groups used to terminate the surface of the nanoparticles form a closely packed layer on the surface and protect the nanoparticle.

Suspensions of the organic terminated nanoparticles have been characterized by photoluminescence spectroscopy. Representative photoluminescence spectra are shown in Figure 3, for both germanium (3a) and Silicon (3b). In Figure 3a the photoluminescence showed a relatively narrow region of intense luminescence with maximum intensity from 400-510 nm, with excitation from 360-460 nm. In Figure 3b the photoluminescence showed a relatively narrow region of intense luminescence with maximum intensity from 400-550 nm, with excitation from 400-460 nm. Though some questions about the photoluminescence spectra remain, the large increase in energy of the photoluminescence relative to the band gap of bulk Ge and Si and the monotonic shift in photoluminescence wavelength with excitation wavelength point to quantum confinement causing the photoluminescence. The increase in photoluminescence intensity from less than 10^{-4} to several percent also reflects quantum confinement predictions.

Size distributions of nanoparticles have conventionally been measured by using Transmission Electron Microscopy (TEM) as shown in Figure 4. Size distributions are usually synthesized in 2-10nm range, however, we have shown that with modification of

the synthesis procedure we can vary the mean size of our samples. To obtain a representative mean size measurement of the bulk sample we used Atomic force Microscopy (AFM) to look at silicon and germanium nanocrystals. Figure 5a shows an AFM image of silicon nanocrystals on mica where the average size measurement is 4nm and 5b where the average size measurement is 2nm.   These mean sizes where obtained by changing the sample preparation conditions.

Conclusions

The reaction between Mg_2T and TCl_4 in refluxing diglyme produced silicon and germanium nanoparticles in high yields, and the surface of these nanoparticles may be terminated using Grignard reagents. Since the particles produced by the initial metathesis reaction are from 2-10 nm in diameter,[15,16] from 10-30 % of their atoms are on the surface. With such a large proportion of atoms at the surface, its termination is vital to controlling their properties. Surface termination with Grignard reagents forms a robust protective layer at the surface of the nanoparticle, and provides an opportunity for further chemical manipulation. Though a considerable amount of work remains, chemically manipulating the surface of the nanoparticles may provide the ability to further tailor their properties and incorporate them into composite materials or devices. The ability to chemically change the surface of the nanoparticles yet retain the luminescence due to quantum confinement is unique to this preparative method. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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Publications

Taylor BR, Fox GA, Hope-Weeks LJ, et al.

Solution preparation of Ge nanoparticles with chemically tailored surfaces,

MAT SCI ENG B-SOLID 96 (2): 90-93 NOV 1 2002 **JC-145430**

 Hope-Weeks LJ, Fox GA, Taylor BR

Preparation of functionalised silicon nanocrystals.

ABSTR PAP AM CHEM S 223: 383-INOR Part 2 APR 7 2002 **UCRL-PRES-146058**

Rev 1

 Taylor BR, Fox GA, Hope-Weeks LJ

Preparation of colloidal germanium nanocrystals with novel surface termination.

ABSTR PAP AM CHEM S 223: 045-COLL Part 1 APR 7 2002

UCRL-PRES-146217
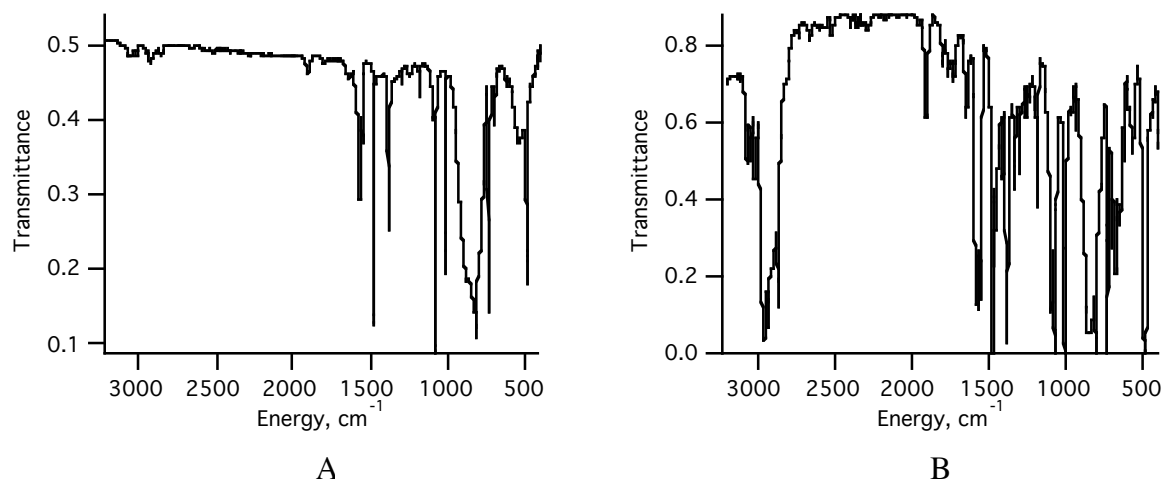
Figure 1. FTIR spectra of p-chlorophenyl terminated Ge nanoparticles. A. Before reaction with propylmagnesium bromide. B. After reaction with propylmagnesium bromide. FTIR spectra were obtained by drying the colloid onto KBr plates.
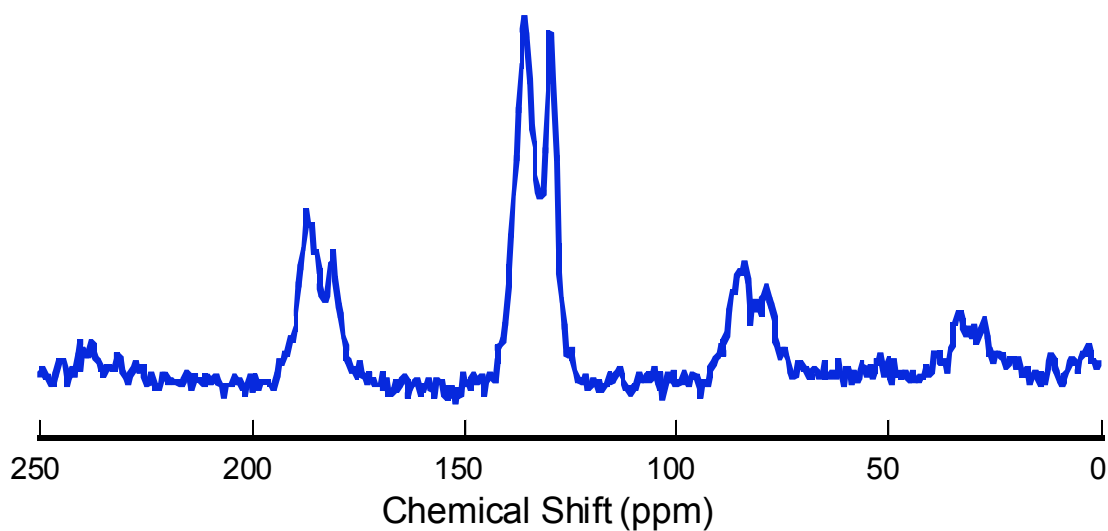

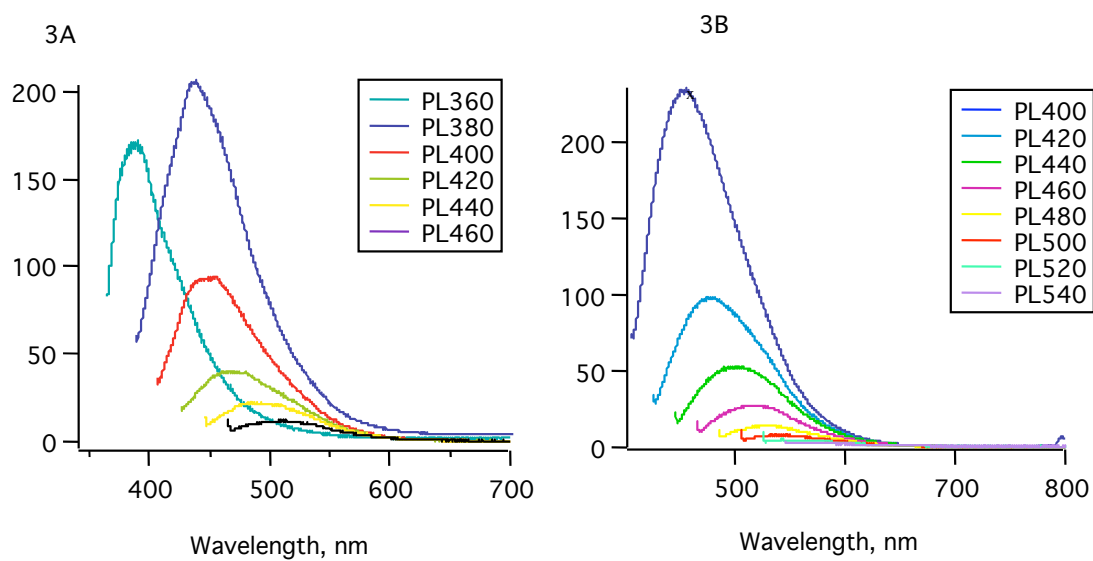Figure 2. Solid-state ^{13}C NMR spectrum of p-chlorophenyl terminated Ge quantum dots.

Figure 3. Photoluminescence spectra. 3A) Germanium nanoparticles with $(C_6H_4)CH_2CH_2CH_3$ groups on the surface 3B) Silicon nanoparticles with $(C_6H_4)Cl$ groups on the surface.
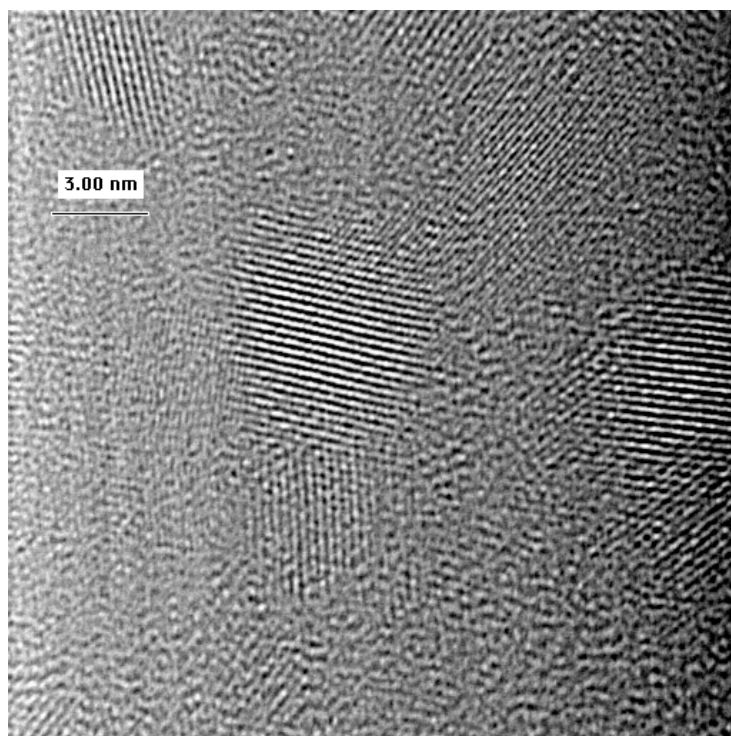

Figure 4. TEM image of germanium nanocrystal. Bright and dark lines are rows of individual atoms in a crystal.
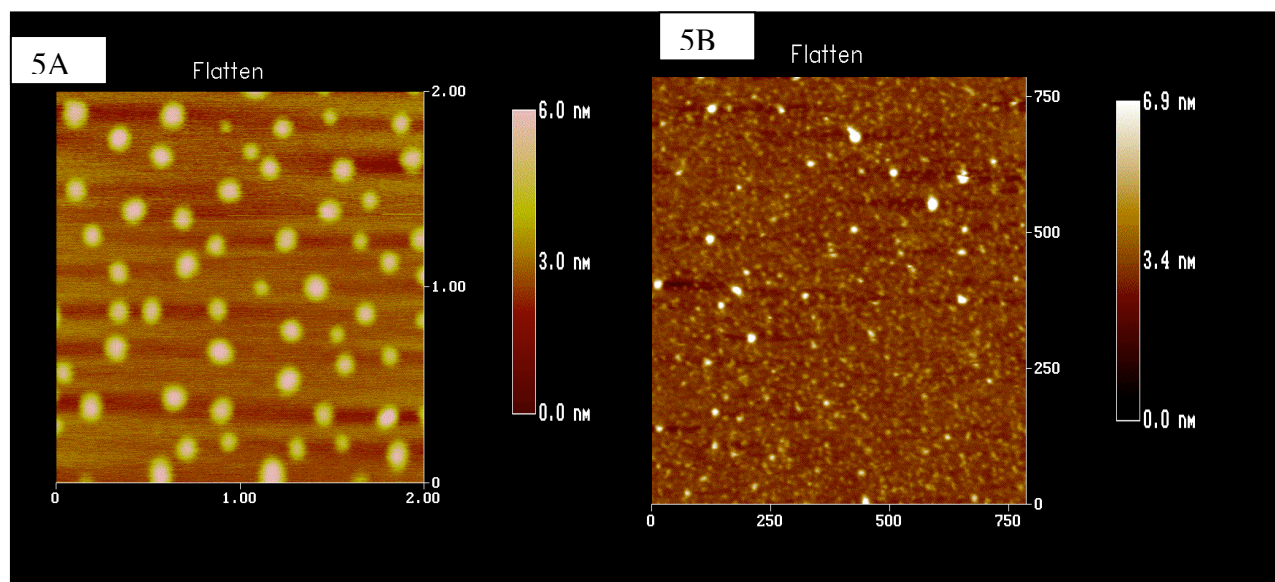
Figure 5. AFM image of Si nanoparticles showing average size distributions of 2nm and 4nm respectively.